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(54) **Detergent additive composition.**

(57) Detergent Additive compositions are disclosed in which a peroxyacid bleach precursor in the form of a substrate particulate having a mean specific area in the range of 0.05 to 0.9 m²/g, is coated with a solid particulate organic acid compound of median particle size <450 micrometers, so as to give a Coating Index value (CI) in the range of from 0.01 to 9. A process for making the additive compositions and detergent products containing them are also disclosed.

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This invention relates to peroxyacid precursor particles, to processes for their manufacture and to detergent compositions containing them. More particularly the invention relates to peroxyacid precursor particles incorporating an acidic coating to provide a delayed start to perhydrolysis of the peroxyacid precursor at the start of a fabric washing cycle in an automatic washing machine.

The incorporation of a peroxyacid precursor as a discrete particulate component of a fabric washing composition is well known in the art. The particulate may comprise the precursor as a crystalline material of the desired particle size as disclosed in GB-A-846798, but a more preferred form comprises an agglomerate of relatively finely divided precursor particles bound together by a binder or agglomerating agent. Examples of this type of precursor particle are discussed in EP-A-0070474, EP-A-0356700, EP-A-0375241 and WO92/13798.

The last named Application also discloses the coating of the agglomerated precursor particle with an acidic material of Mpt $> 30^{\circ}\text{C}$ and defined minimum aqueous solubility at 20°C , in order to provide a low pH environment during the initial stages of dissolution/dispersion of the agglomerate in the aqueous wash pre-liquor. A low pH environment in the immediate vicinity of the peroxyacid precursor particle during the product dissolution/dispersion stage of the wash cycle prevents or minimises colour damage to fabrics, particularly where so called concentrated or 'compact' detergent compositions are employed.

WO92/13798 teaches that the coating of acidic material should be applied as a melt for those acidic materials having of Mpt $< 100^{\circ}\text{C}$ and as a solution or dispersion for acidic materials of Mpt $> 100^{\circ}\text{C}$. Electrostatic Powder coating is also mentioned as a possible technique of applying the acidic material to the agglomerate but is discounted on the grounds of difficulty and expense.

Powder coating of an agglomerated particle containing a peroxyacid precursor is also disclosed in EP-B-0191396. A powder of fine-grained material of particle size 0.1-1mm is applied to the surface of an agglomerate of particle size 0.4-4mm and comprising a powder or fine grained component and at least 20% of a liquid component to give a dry, free flowing granulate.

Notwithstanding the advances in the art represented by the above disclosures, difficulties have still been encountered in providing peroxyacid precursor particles having acceptable physical characteristics for bulk storage and handling, whilst at the same time providing the desired low pH environment on dissolution/dispersion. Moreover, where a peroxyacid precursor of Mpt $< 100^{\circ}\text{C}$ is employed, the application of an acidic coating material as a melt may not be feasible and its application as an aqueous or solvent solution may result in significant capital and/or operating expense for drying and/or solvent recovery.

The Applicant has now found that these problems can be overcome by the provision of a peroxyacid precursor particle having a coating formed of a particulate water soluble organic acid compound of a selected particle size range, where the proportion of the surface of the peroxyacid precursor particles that is coated is controlled so as to lie within a defined range. This finding was particularly surprising in the case of the preferred organic acid compounds, in view of their known hygroscopicity. In addition the provision of a particulate coating of an organic acid material on the peroxyacid precursor particles has been found to enhance the stability of perfume components in detergent products incorporating the detergent additive compositions.

According to one aspect of the present invention there is provided a solid detergent additive composition comprising a surface treated particulate, said particulate forming a substrate having a mean specific surface area in the range of from 0.05 to $0.9\text{ m}^2/\text{g}$ and comprising a peroxyacid bleach precursor, said precursor containing one or more N- or O- acyl groups, the external surfaces of said substrate particulate being treated with and bearing a solid water soluble organic acid compound having a Mpt $> 30^{\circ}\text{C}$, said solid water soluble organic acid compound being in the form of plurality of discrete coating particles adhered to the external surface of each substrate particle, wherein the discrete coating particles have a median particle size of no greater than 450 micrometers and wherein the surface treated particulate has a Coating Index value, defined by the ratio of the area of the coated external surface of the substrate to the area of the uncoated external surface of the substrate, in the range of from 0.01 to 9.

Preferably the Coating Index value lies in the range of from 0.1 to 2 and more preferably in the range of from 0.2 to 1.

Preferably the median particle size of the acidic coating material is < 150 micrometers and more preferably < 100 micrometers. Most preferably the median particle size is < 50 micrometers. Preferably the peroxyacid precursor has a Mpt $< 120^{\circ}\text{C}$, more preferably $< 100^{\circ}\text{C}$ and most preferably $< 80^{\circ}\text{C}$.

In a further aspect of the invention a process for making a solid detergent additive composition comprises the steps of:

- a) providing a solid peroxyacid bleach precursor material containing one or more N- or O- acyl groups having a Mpt $> 30^{\circ}\text{C}$, said material being in the form of a mass of particles of median size < 150 micrometers;

b) mixing therewith a solid organic binder material having a melt point $>10^{\circ}\text{C}$ below the lower of the melting point or decomposition temperature of the bleach precursor;

c) treating said mixture to form agglomerates having a mean specific area in the range of from 0.05 to $0.9\text{ m}^2/\text{g}$;

d) maintaining said agglomerates at a temperature above the softening point of the organic binder material;

e) treating said agglomerates with a particulate water soluble organic acid compound of median particle size no greater than 450 micrometers; and

f) reducing the temperature of said treated agglomerates to a value of 10 to 25°C to cause a plurality of discrete particles of said acid compound to adhere to the external surfaces of each of the agglomerates thereby to give a Coating Index value, defined by the ratio of coated to uncoated surface area of the agglomerate, in the range of from 0.01 to 9.

Preferably, the temperature in steps d) and e) is chosen so as to provide an agglomerate in which 0.1% to 5% by weight of the agglomerate is not solid, in order to ensure adherence of the particulate acid compound to the agglomerate.

For the purposes of the present invention the Melting Point and Softening Point temperatures are defined as follows:

The Softening Point is the temperature at which the material starts to lose its physical integrity, i.e. starts to deform.

The Melting Point is defined as the temperature at which the liquid fraction of the material forms a continuous phase in which the remainder is dispersed.

In a yet further aspect of the present invention a detergent composition is provided comprising a surfactant material, a source of alkaline hydrogen peroxide and a particulate detergent additive composition as hereinbefore defined, or as made by the process as hereinbefore defined.

The invention also relates to certain peroxyacid precursor particulates of enhanced visual appearance.

Peroxyacid precursor materials useful in the present invention are compounds containing one or more N- or O- acyl groups. These can be selected from a wide range of classes that include anhydrides, esters, imides and acylated derivatives of imidazoles and oximes, and examples of useful materials within these classes are disclosed in GB-A-1586769.

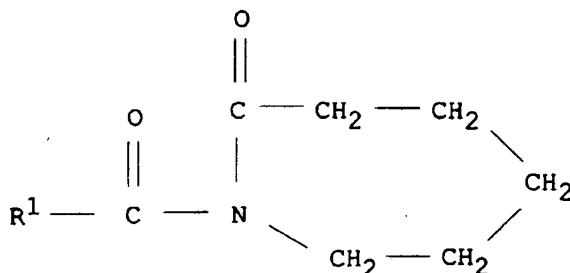
Peroxyacid precursor particulates containing mixtures of any of the precursors hereinafter disclosed are also contemplated by the present invention.

Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386. Specific O-acylated precursor compounds of this type include 2,3,3-tri-methyl hexanoyl oxybenzene sulfonates, benzoyl oxybenzene sulfonates, nonanoyl-6-amino caproyl oxybenzene sulfonates, and penta acetyl glucose.

Useful N-acyl compounds are disclosed in GB-A-855735, 907356 and GB-A-1246338. Preferred precursor compounds of the imide type include N-benzoyl succinimide, tetrabenzoyl ethylene diamine, N-benzoyl substituted ureas and the N-,N,N',N' tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms.

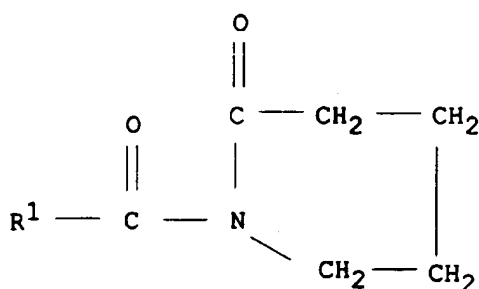
N-acylated precursor compounds of the lactam class are disclosed generally in GB-A-855735. Whilst the broadest aspect of the invention contemplates the use of any lactam useful as a peroxyacid precursor, preferred materials comprise the caprolactams and valerolactams.

Suitable caprolactam bleach precursors are of the formula:



wherein R¹ is H or an alkyl, aryl, alkoxyaryl or alkaryl group containing from 1 to 12 carbon atoms, preferably from 6 to 12 carbon atoms.

Suitable valero lactams have the formula:



wherein R¹ is H or an alkyl, aryl, alkoxyaryl or alkaryl group containing from 1 to 12 carbon atoms, preferably from 6 to 12 carbon atoms. In highly preferred embodiments, R¹ is selected from phenyl, heptyl, octyl, nonyl, 2,4,4-trimethylpentyl, decenyl and mixtures thereof.

The most preferred materials are those which are normally solid at <30°C, particularly the phenyl derivatives, i.e. benzoyl valerolactam, benzoyl caprolactam and their substituted benzoyl analogues such as chloro, amino alkyl, alkyl, aryl and alkoxy derivatives.

Caprolactam and valerolactam precursor materials wherein the R¹ moiety contains at least 6, preferably from 6 to about 12, carbon atoms provide peroxyacids on perhydrolysis of a hydrophobic character which afford nucleophilic and body soil clean-up. Precursor compounds wherein R¹ comprises from 1 to 6 carbon atoms provide hydrophilic bleaching species which are particularly efficient for bleaching beverage stains. Mixtures of 'hydrophobic' and 'hydrophilic' caprolactams and valero lactams, typically at weight ratios of 1:5 to 5:1, preferably 1:1, can be used herein for mixed stain removal benefits.

Suitable imidazoles include N-benzoyl imidazole and N-benzoyl benzimidazole and other useful N-acyl group-containing peroxyacid precursors include N-benzoyl pyrrolidone, dibenzoyl taurine and benzoyl pyroglutamic acid.

Where the precursor materials are liquid at ambient temperature or at temperatures likely to be encountered during storage of the materials prior to use, i.e. at temperatures up to 40°C, they are adsorbed onto solid organic materials used as agglomerating agents so as to enable the formulation of a particulate substrate material. The preferred peroxyacid precursors for the present invention have a Mpt > 30°C and preferably > 40°C. Such precursors will normally be fine powder form, having been derived by crystallisation from a solvent medium or by spray drying from a solvent medium or from a molten state. Preferably at least 90% by weight of the powder has a particle size of > 150 micrometers.

This powder can be surface treated directly but is more usually combined with other detergent ingredients, prior to surface treatment, to form the substrate particulate material. One preferred method of combining the peroxyacid precursor and other such ingredients is by agglomeration. The resultant particulate material should preferably have a size distribution such that at least 85%, preferably at least 90% by weight thereof has a particle size between 250 and 1200 micrometers, corresponding to a specific area of from 0.05 to 0.9 m²/g.

Suitable binders or agglomerating agents for both solid and liquid peroxyacid precursor materials include C₁₂-C₁₈ fatty acids, C₁₂-C₁₈ aliphatic alcohols condensed with from 10 to 80 moles of ethylene oxide per mole of alcohol, polyethylene glycols of MW 4000 - 10000 and polymeric materials such as polyvinyl pyrrolidone.

The agglomerating agent is incorporated at levels of from 5% to 50% by weight of the particulate to be agglomerated, more preferably from 5% to 25% by weight and most preferably from 10% to 15% by weight. The preferred solid peroxyacid precursors normally require weight percentages of agglomerating agent at the lower end of the range.

In the broadest aspect of the invention the peroxyacid precursor material has a structure that perhydrolyses in the aqueous wash liquor to provide stain removal over a spectrum of oxidisable stains on substrates exposed to the wash liquor. However, the invention also contemplates the use of two or more such materials each producing oxidising species having differing stain removal profiles. Thus the invention includes precursor compositions containing combinations of precursors of peroxyacids having bulk solution

stain removal capability and precursors of peroxyacids having the ability to bleach transient stain material (eg. dyes transferred during the wash process) and/or precursors of fabric surface substantive peroxyacids. Combinations of peroxyacid precursors together with organic peroxides having enhanced stain removal capability on vegetable stains such as carotene are also included.

5 Other additives that are compatible with the peroxyacid precursors may also be included in detergent additive compositions in accordance with the invention. Examples of such additives include surfactants, fluorescers, enzymes, suds suppressors, dye transfer inhibition agents, soil suspending agents, water soluble builders and chelating agents and water-insoluble inorganic compounds of high specific area. Specific embodiments of such additives and their levels of incorporation are described hereinafter but the
10 total level of the additives normally lies in the range of from 5% to 50% by weight of the additive composition. The peroxyacid precursor(s) should form the major component of the precursor composition, ie. from 50% to 95% by weight of the agglomerate, preferably at least 55% by weight and most preferably at least 60% by weight thereof.

One preferred material for incorporation in the agglomerated embodiments of the detergent additive
15 compositions of the invention is a solid water soluble organic or inorganic acid compound, present in an amount of from 3% to 35% by weight of the composition more preferably in an amount of from 5% to 30% and most preferably from 10% to 25% by weight. For the purposes of the invention an acid compound is defined as a compound that, in a 1% solution in distilled water at 20 °C, has a pH of 6.5 or less. Also for the purposes of the invention, 'a solid' is defined as material that is a solid at ambient temperatures, and so
20 organic acid compounds must have a Melting Point of at least 30 °C and preferably of at least 40 °C. Preferred organic acid compounds will have a Melting Point in excess of 50 °C.

The acid compound must also be highly soluble in water at ambient temperatures, highly soluble being defined for the purposes of the present invention as at least 5g of the acid dissolving in 100g of distilled water at 20 °C. Preferably the acid compound has a solubility of at least 20g/100g of water at 20 °C and
25 most preferably the acid compound will dissolve in its own weight of water at 20 °C.

Inorganic acid compounds suitable for incorporation in the agglomerated embodiments of the invention include the alkali metal hydrogen sulphates, acid pyrophosphates and acid orthophosphates. Organic acid compounds, which are preferred, include citric acid and the acid citrate salts, glycolic acid, polyacrylic acid of MWt 500 - 20,000 and acid copolymers of maleic anhydride and acrylic acid of MWt 500 - 100,000.

30 It has also been observed that detergent additive compositions in accordance with the invention that contain an acid compound, particularly an organic acid compound, in the peroxyacid precursor substrate particulate exhibit superior compatibility (versus compositions without acid coating and acid coagglomerates), with perfumes, stilbene based optical brighteners such as TINOPAL DMS, aminophosphonate and aminocarboxylate chelants, enzymes, fatty amino fabric softeners and surfactants based on fatty acids,
35 eg. oleyl sarcosinate and oleyl alkyl sulfate.

Another optional but preferred component of agglomerated or spray-dried detergent additive compositions of the invention is a water-insoluble inorganic compound of surface area 2-4m²/g, present in an amount of from 1% to 15% by weight of the agglomerate, more preferably from 2% to 10% by weight. The presence of the water insoluble inorganic compound improves the flow characteristics for the resultant
40 agglomerate or spray dried particle. Preferred examples of such inorganic compounds are aluminosilicates, particularly the synthetic zeolites known as Zeolite A, X, P & MAP, and natural aluminosilicates such as montmorillonite, hectorite and saponite of the smectite class of clay minerals.

The substrate particulate may be formed by spray drying an aqueous slurry of the peroxyacid precursor and other preferred non heat sensitive components, such as an organic acid compound, optical brighteners,
45 chelants, soil suspending agents and dye transfer inhibition agents. Heat sensitive components such as enzymes and suds suppressors are not preferred components of substrate particulates made in this manner.

In those embodiments of the invention where the substrate particulate comprises an agglomerate of the peroxyacid precursor, the agglomeration process may be any of those well known in the art. Thus the use
50 of Glatt fluidised bed granulation or Lodige, Eirich or Fuji mixing equipment is contemplated for the production of such agglomerates under appropriate conditions.

Where the precursor is a solid, it is conventionally supplied in the form of a fine powder. This can be handled without difficulty where the material has a Mpt > 100 °C but powdered organic material of
55 Mpt < 100 °C frequently has poor particle flow characteristics. Conversion of the material into a thin flake form overcomes this problem.

Benzoyl caprolactam, a preferred bleach precursor useful in the present invention, has a Mpt in the range 65 - 70 °C and is conventionally crystallised from a molten mother liquor and filtered to provide a fine powder. The crystallisation and filtration steps can be replaced by a cooling step using a rotating chill roll

partially immersed in a dip tray of molten benzoyl caprolactam. An applicator roll, positioned against the chill roll on the coated surface leaving the dip tray, applies a shear force to the coating that encourages crystallisation of the thin layer of benzoyl caprolactam picked up by the chill roll. Optimisation of the temperatures of the two rolls permits control of the coating thickness to a value in the range 0.5 - 2.0 mm. A doctor knife is then used to remove the solidified coating from the chill roll as separate flakes.

A typical peroxyacid precursor agglomerate comprises a mixture of benzoyl caprolactam and citric acid particles each having a mean particle size <150 micrometers in a ratio of 80:20 by weight which is agglomerated with from 15-20% of polyethylene glycol of MWt 4000 in a Lodige KM mixer to provide an agglomerate of mean particle size 550 to 600 micrometers and particle size distribution such that 95% of the particles lie in the range from 250 micrometers to 1200 micrometers. An unexpected advantage of this particulate is a colour improvement arising from the agglomeration of the peroxyacid precursor. A determination of L, a & b values using a Hunter Colour Meter on a sample of the benzoyl caprolactam of median particle size 260 micrometers and on a sample of the agglomerate composition described hereinabove with a particle size in the range of 250 micrometers to 1200 micrometers gave the following results:

	L	a	b
Precursor	83.6	0.3	9.1
Agglomerate	85.8	-0.3	8.6

The increase in L and decrease in b value for the agglomerate relative to the precursor shows a significant colour improvement.

Another preferred peroxyacid precursor agglomerate comprises an intimate mixture of powdered benzoyl caprolactam (particle size <50 μm) with a powdered partially neutralised maleic anhydride acrylic acid copolymer (MWt \approx 70,000) (particle size <50 μm), the weight ratio of benzoyl caprolactam to copolymer being 90:10, the mixture being agglomerated with from 15-20% by weight of the mixture of polyethylene glycol of MWt 4000 to give an aggregate of mean particle size 500-600 μm . This precursor agglomerate has a pH in 1% solution of from 4-7 and shows improved stability in detergent materials.

In general, the peroxyacid precursor particulate is formed to have a particle size such that it has a mean specific area, ie. a surface area per g weight, in the range of from 0.05 m^2/g to 0.9 m^2/g , preferably from 0.1 m^2/g to 0.5 m^2/g . This requirement is normally satisfied for spherical particles by a particle size in the range from 250 micrometers to 1200 micrometers and at least 85% by weight of the agglomerate should fall within this range. More preferably the particle size should be in the range of from 250 micrometers to 750 micrometers and most preferably from 550 micrometers to 650 micrometers providing a specific area in the range from 0.2 m^2/g to 0.3 m^2/g .

Specific area is measured, for the purposes of the present invention, by the following technique.

The specific surface area, of peroxyacid precursor particulate, is measured using Physisorption equipment comprising of a Micromeritics Gemini 2360 analyser, a Flow prep 060 sample handler and printer.

This equipment is manufactured by Micromeritics Instrument Corporation, One Micromeritics Drive, Norcross GA 30093-1877, USA.

For this analysis a Flow prep sample container is filled, up to the marked line, with a known weight (to 4 dp (decimal places)) of particulate material. This is then placed in the heating station of the equipment, which is preset to the highest temperature at which the particulate is thermodynamically stable. A gas delivery tube is inserted in the sample tube and held in position with a bung. The sample is then left for two hours to degas.

While the test sample is degassing, the saturation pressure (P_0) in mm of Hg is determined and stored in the Gemini analyser, using a Balance tube and filler rod in the left (reference) port and an empty tube in the right (sample) port, of the Gemini.

After degassing, the sample tube is reweighed to determine the final weight of particulate material. It is then filled with a filler rod and placed in the sample port of the analyser. The sample is then analysed at five points over a range of relative pressures between 0.05 to 0.30 P/P_0 where P is the sample pressure. The analyser provides a direct reading of the specific surface area of the particle in m^2/g .

In preferred agglomerate embodiments of the invention the diameter of the pores forming the spaces between the agglomerated particles is selected by controlling the levels of compaction and shear applied during the agglomeration process. Too large a pore size results in an agglomerate of inadequate strength and a tendency to disintegrate during handling. Too small a pore size results in an agglomerate having a

slow rate of dissolution. It has been found that a satisfactory agglomerate has a porosity corresponding to a mean pore diameter in the range of from 3 to 6 micrometers. The porosity is measured according to the following technique, using a Micromeritics Poresizer 9320.

This equipment is manufactured by Micromeritics Instrument Corporation, One Micromeritics Drive, Norcross GA 30093-1877, USA and comprises a Penetrometer, Analyser and printer.

For this analysis the Penetrometer bulb is filled with a known weight (to 4dp) of particulate material. The Penetrometer is then fully assembled with the insulator seal, spring and retaining collar. This is then fitted into the low pressure port of the porosity analyser. The Penetrometer is then evacuated and the sample analysed under the following set point conditions:

Maximum measurable volume	0.387 ml
Total stem volume	0.412 ml
Maximum head pressure	4.68 psi (porosity pressure readings)
Penetrometer constant	10.79 l/pf (litres/pico farad)

at the following pressures: 2, 3, 4, 5.5, 7, 8.5, 10.5, 13, 16, 20, 23, 25 psia.

After this analysis the Penetrometer bulb is installed in the high pressure chamber and analysed under the same set point conditions and the printer then gives the median pore diameter and pore intrusion volumes for the sample. For the preferred pore diameter of 3-6 micrometers, the pore intrusion volume is in the range 0.07 to 0.1 ml/g.

The solid detergent additive composition aspect of the invention is characterised by the presence of discrete particles of a solid water soluble organic acid compound adhered to the external surfaces of the peroxyacid precursor particulate so as to provide a Coating Index value of from 0.01 to 9 preferably from 0.1 to 2. The organic acid compound must satisfy several criteria.

Firstly, it must be a solid at ambient temperatures and so must have a Melting Point of at least 30 °C and preferably of at least 40 °C. Preferred organic acid compounds will have a Melting point in excess of 50 °C.

Secondly, the organic acid compound must also be highly soluble in water at ambient temperatures, highly soluble being defined for the purposes of the present invention as at least 5g of the acid dissolving in 100g of distilled water at 20 °C. Preferably the organic acid compound has a solubility of at least 20g/100g of water at 20 °C and most preferably the organic acid compound will dissolve in its own weight of water at 20 °C.

Thirdly, the organic acid compound must have a median particle size <450 micrometers, preferably less than 250 micrometers, more preferably less than 150 micrometers. Highly preferred coating particles have a median particle size of less than 100 micrometers, with the most preferred median particle size being less than 50 micrometers.

Organic acid compounds suitable as treating agents for the purposes of the present invention comprise aliphatic or aromatic carboxylates. The carboxylates may be monomeric, oligomeric or polymeric in nature and preferably comprise aliphatic carboxylic acids. Examples of monomeric aliphatic acid compounds are glycolic, glutamic, citraconic, succinic, L-lactic and citric acids. Examples of polymeric acid compounds include poly(meth)acrylic acids and copolymeric derivatives with maleic anhydride. Preferred monomeric acids are citric and glycolic acids while preferred polymeric acids include polyacrylic acids of MWt 3000-5000, especially about 4500 and acrylic acid maleic anhydride copolymers of MWt 40000-90000.

The acids are applied at levels of from 2% to 20% by weight of the precursor particulate, more preferably from 2% to 15% and most preferably from 3% to 10% by weight of the treated particulate. Citric acid or maleic anhydride acrylic acid copolymer at a level of approximately 7% by weight of the treated particulate is a particularly preferred surface treating agent.

The coating index (CI) is defined as

$$\frac{\text{Area of substrate covered by dusting}}{\text{Area of substrate not covered by dusting}}$$

which can be written as

Total cross sectional area covered by dusting (Sc)

$$\text{Total surface area of substrate (Ss) - Total cross sectional area covered by dusting (Sc)}$$

5

Or

10

$$CI = \frac{Sc}{Ss - Sc}$$

15 The following calculations assume that the coating and substrate particles are spherical and that each "coating particle" covers an area of substrate particle represented by the projection, on the substrate particle in the region of mutual contact, of the maximum cross sectional surface area of the coating particle in a plane parallel to that of the substrate particle.

Total surface area of the substrate particles

20

$$(Ss) = Ns 4\pi \left[\frac{Ds}{2} \right]^2 = Ns \pi Ds^2$$

where

Ds is the median particle size of the substrate particle in micrometers and

25 Ns is the number of substrate particles in 100g of coated agglomerates.

Ns can be calculated as

30

$$\frac{\text{Total volume of substrate}}{\text{Volume of one substrate particulate}} = \left[\frac{Ms}{\rho_s} \right] / \frac{4\pi}{3} \left[\frac{Ds}{2} \right]^3 = \frac{6Ms}{\rho_s \pi Ds^3}$$

where

35 ρ_s is the absolute density of the substrate particle

and

Ms is the mass of substrate particles per 100g of coated agglomerates

40

$$Ss = \frac{6Ms \pi Ds^2}{\rho_s \pi Ds^3} = \frac{6Ms}{\rho_s Ds}$$

45 Total cross sectional area of the coating particles

50

$$(Sc) = Nc \pi \left[\frac{Dc}{2} \right]^2 = \frac{Nc \pi Dc^2}{4}$$

where

Dc is the median particle size of the coating particle in micrometers

55 and

Nc is the number of coating particles in 100g of coated agglomerates

Nc can be calculated as

$$\frac{\text{Total volume of dusting}}{\text{Volume of one dusting particulate}} = \left[\frac{Mc}{\rho c} \right] \div \frac{4\pi}{3} \left[\frac{Dc}{2} \right]^3 = \frac{6Mc}{\rho c \pi Dc^3}$$

where

ρc is the absolute density of the coating particle

and

10 Mc is the mass of coating particles per 100g of coated agglomerates

$$Sc = \frac{6\pi Dc^2 Mc}{4\pi \rho c Dc^3} = \frac{1.5Mc}{\rho c Dc}$$

This gives a final equation for the coating index of:

$$CI = \frac{1.5 Mc}{\rho s Ds} \div \left[\left[\frac{6Ms}{\rho s Ds} \right] - \left[\frac{1.5 Mc}{\rho c Dc} \right] \right]$$

Generally, the weight of acid coating (Mc) can be established by dissolving a known weight of the coated particles in a known quantity of an appropriate solvent medium, determining the molar concentration of the acid compound and converting this to a number of moles for a unit weight of coated particles.

30 Where the substrate particle includes an organic acid compound, and particularly where this is the same as the acid coating material, an indirect method of calculating the coating weight can be used. The lithium salt of the acid coating compound is prepared in a particular form having the same particle size distribution and mean particle size as the acid coating material itself. The value for Mc can be found by substituting particles of the lithium salt of the coating acid compound for the acid compound itself in the
35 coating process, under identical conditions of substrate particle temperature, weight of coating particles per kg substrate particle, time of mixing and agitation. The weight percentage of lithium associated with the particle (MLi) is then directly measured by Atomic Adsorption analysis.

In the preferred embodiment of the present invention where Citric acid is coagglomerated with the peroxyacid precursor and also forms the acid coating compound, Trilithium Citrate can be substituted for
40 the Citric acid in order to permit establishment of the CI value under a predetermined set of conditions.

$$\text{Thus the coating weight (Mc)} = \frac{MLi \text{ MWLi Citrate}}{MWLi}$$

where $MWLi$ Citrate is the molecular weight of Lithium Citrate hydrate and $MWLi$ is the molecular weight of Lithium.

50 The weight of substrate (Ms) can also be determined as $Ms = 100Mc$. These along with the analysed values for median particle size and density of both the substrate and the coating can be substituted into the Coating index equation and the coating index therefore determined.

For the purposes of the present invention the CI value should lie between 0.01 and 9, preferably between 0.1 and 2.0 and most preferably between 0.2 and 1.0. The minimum CI value defines the minimum
55 amount of coating of the substrate particle to provide a transient low pH environment around the particle on immersion in a wash liquor. This low pH environment results in a delay in the initiation of perhydrolysis where alkaline hydrogen peroxide is present in the wash liquor and avoids or minimises damage to fabrics in the vicinity of the peroxyacid precursor particle. Additionally CI values of 0.4 or more provide coated

peroxyacid precursor particles with the desired flow characteristics in bulk. CI values in excess of 9 lead to an unnecessarily large delay to the start of perhydrolysis on dissolution of the particle, and may result in undesirable levels of moisture pick up where hygroscopic acid coating materials are used. CI values > 2.0 are less cost effective and may also have an adverse effect of the flow and handling characteristics of the coated particle.

The surface treatment of the peroxyacid precursor particulate can be carried out in a number of ways using equipment known in the art and the process may take place in batch wise or continuous fashion. In a batch process to make the preferred agglomerate embodiments of the invention, an Eirich or Lodge FM agglomeration is used whilst the continuous process can utilise a Shugi Mixer or a Lodge CB or KM Mixer.

A combination of the Lodge CB and KM Mixers is preferred.

A typical powder coated agglomerate formulation comprises:

Bleach Activator (100μ)	50 to 95%
Acid Agglomerating Agent (50μ)	0 to 50%
Binder	5 to 25%
Acid powder coating (50μ)	up to 10%

The powdered materials, viz. the bleach activator and the acid agglomerating agent are fed to the agglomerator at a temperature between 20 °C and 30 °C. The binder, which is preferably a Tallow alcohol condensed with from 11 to 50 moles of ethylene oxide per mole, or a Polyethylene glycol of MWt 1000 to 8000, is then fed to the agglomerator as a molten material at approximately 55 °C. The binder is added over a period of from 30 to 60 seconds and the mass is then mixed for a further 1 to 2 minutes, the temperature of the mixture being approximately 30 to 35 °C.

The acid powder coating is then applied to the mixture and the temperature of the agglomerates is maintained in the range 30 °C-35 °C while the agglomerates and powder are mixed for a period of up to 60 seconds, preferably from 15-30 seconds. This is normally sufficient to cause the powder coating to adhere to the exterior surfaces of the agglomerates. Selection of the appropriate coating temperature for any specific agglomerate composition can be undertaken by reference to a Differential Scanning calorimetry curve for the composition.

The mixing is then stopped and the detergent additive composition is cooled to ambient temperature (15-25 °C) by means of techniques known in the art, eg. fluid bed cooling with an air inlet temperature of 5-15 °C. Control of coating powder particle size, agglomerate temperature and residence time in the mixer provide a detergent additive composition with the desired level of coating as represented by the Coating Index value.

A preferred optional component of the detergent additive compositions of the invention is a dusting agent used at a level of from 1% to 5% by weight, particularly for those compositions incorporating bleach precursors of Mpt<120 °C, and even more particularly such precursors in agglomerated form. This dusting component improves the flow of the detergent additive compositions and preferably takes the form of a water-insoluble inorganic compound of particle size <50 micrometers, preferably 1-10 micrometers. Examples of such compounds include the synthetic zeolites and hydrophobic silicas. Application of the dusting agent can take place with or after the application of the powdered organic acid compound.

The powder coated additive products of the present invention can be further modified by the application of a slow dissolving or a hydrophobic coating that delays the dissolution/dispersion and subsequent perhydrolysis of the bleach precursor. Suitable coating materials are well known and include C₂₀-C₂₄ fatty acids, high Mpt nonionic surfactants, waxes and polymer or latex solutions. Such coatings would be applied at a level of from about 1% to about 20% by weight of the additive product particle, dependent on the required delay in dissolution/dispersion and the nature of the coating material.

The detergent composition aspect of the invention comprises the incorporation of the hereinbefore described solid additive compositions together with a surfactant material, a source of alkaline hydrogen peroxide, and optionally other detergent ingredients, in a granular detergent product.

The preferred application for the solid detergent additive compositions of the invention is as particulate components of the so-called concentrated detergent compositions that are added to a washing machine by means of a dosing device placed in the machine drum with the soiled fabric load. Concentrated granular detergent compositions dispensed into the wash liquor via a dosing device are more subject to dissolution problems than compositions added via the dispensing compartment of a washing machine because, in the initial stages of a wash cycle, the agitation in the immediate environment of the product is inhibited by the presence of the fabric load. Whilst this can constitute a benefit in permitting the development of high

transient concentrations of builder and surfactant, the development of high transient peroxyacid concentrations can, as noted previously, lead to fabric and colour damage. The detergent additive compositions of the present invention, when incorporated into concentrated detergent products delivered to the wash liquor via a dispensing device, mitigate if not eliminate this problem.

5 Detergent compositions incorporating the surface treated peroxy acid bleach precursor particulates will normally contain from 0.5% to 12% of the precursor, more frequently from 1% to 10% and most preferably from 2% to 9%, on a composition weight basis.

Such detergent compositions will, of course, contain a source of alkaline hydrogen peroxide necessary to form a peroxyacid bleaching species in the wash solution and preferably will also contain other components conventional in detergent compositions. Thus preferred detergent compositions will incorporate 10 one of more of surfactants, organic and inorganic builders, soil suspending and anti-redeposition agents, suds suppressors, enzymes, fluorescent whitening agents photo activated bleaches, perfumes and colours.

Detergent compositions incorporating the surface treated particulate peroxyacid precursors of the present invention will include an inorganic perhydrate bleach, normally in the form of the sodium salt, as the 15 source of alkaline hydrogen peroxide in the wash liquor. This perhydrate is normally incorporated at a level of from 3% to 40% by weight, more preferably from 5% to 35% by weight and most preferably from 8% to 30% by weight of the composition.

The perhydrate may be any of the alkali metal inorganic salts such as perborate monohydrate or tetrahydrate, percarbonate, perphosphate and persulfate salts, but is conventionally an alkali metal perborate 20 or percarbonate. Whilst fabric colour damage arising from compositions in accordance with the invention is low, irrespective of whether a perborate or percarbonate salt is employed, the improvement in comparison with uncoated precursor particulates is more noticeable with percarbonate bleach as this causes greater fabric colour damage in the absence of any coating on the bleach precursor.

Sodium percarbonate, which is the preferred perhydrate, is an addition compound having a formula 25 corresponding to $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$, and is available commercially as a crystalline solid. Most commercially available material includes a low level of a heavy metal sequestrant such as EDTA, 1-hydroxyethylidene 1, 1-diphosphonic acid (HEDP) or an aminophosphonate, that is incorporated during the manufacturing process. For the purposes of the detergent composition aspect of the present invention, the percarbonate can be incorporated into detergent compositions without additional protection, but preferred executions of 30 such compositions utilise a coated form of the material. A variety of coatings can be used including borosilicate borate, boric acid and citrate or sodium silicate of $\text{SiO}_2:\text{Na}_2\text{O}$ ratio from 1.6:1 to 3.4:1, preferably 2.8:1, applied as an aqueous solution to give a level of from 2% to 10%, (normally from 3% to 5%) of silicate solids by weight of the percarbonate. However the most preferred coating is a mixture of sodium carbonate and sulphate or sodium chloride.

35 The particle size range of the crystalline percarbonate is from 350 micrometers to 1500 micrometers with a mean of approximately 500-1000 micrometers.

A wide range of surfactants can be used in the detergent compositions. A typical listing of anionic, nonionic, ampholytic and zwitterionic classes, and species of these surfactants, is given in USP 3,929,678 issued to Laughlin and Heuring on December, 30, 1975. A list of suitable cationic surfactants is given in 40 USP 4,259,217 issued to Murphy on March 31, 1981.

Mixtures of anionic surfactants are suitable herein, particularly blends of sulphate, sulphonate and/or carboxylate surfactants. Mixtures of sulphonate and sulphate surfactants are normally employed in a sulphonate to sulphate weight ratio of from 5:1 to 1:2, preferably from 3:1 to 2:3, more preferably from 3:1 45 to 1:1. Preferred sulphonates include alkyl benzene sulphonates having from 9 to 15, especially 11 to 13 carbon atoms in the alkyl radical, and alpha-sulphonated methyl fatty acid esters in which the fatty acid is derived from a $\text{C}_{12}\text{-C}_{18}$ fatty source, preferably from a $\text{C}_{16}\text{-C}_{18}$ fatty source. In each instance the cation is an alkali metal, preferably sodium. Preferred sulphate surfactants in such sulphonate sulphate mixtures are alkyl sulphates having from 12 to 22, preferably 16 to 18 carbon atoms in the alkyl radical.

Another useful surfactant system comprises a mixture of two alkyl sulphate materials whose respective 50 mean chain lengths differ from each other. One such system comprises a mixture of $\text{C}_{14}\text{-C}_{15}$ alkyl sulphate and $\text{C}_{16}\text{-C}_{18}$ alkyl sulphate in a weight ratio of $\text{C}_{14}\text{-C}_{15}:\text{C}_{16}\text{-C}_{18}$ of from 3:1 to 1:1.

The alkyl sulphates may also be combined with alkyl ethoxy sulphates having from 10 to 20, preferably 10 to 16 carbon atoms in the alkyl radical and an average degree of ethoxylation of 1 to 6. A particularly preferred anionic surfactant system embodying such a combination comprises a mixture of a $\text{C}_{14}\text{-C}_{15}$ alkyl 55 sulphate and an ethoxylated $\text{C}_{12}\text{-C}_{15}$ alkyl sulphate containing an average of about three ethylene oxide groups per moles. The cation in each instance is again an alkali metal, preferably sodium.

Other anionic surfactants suitable for the purposes of the invention are the alkali metal sarcosinates of formula

R-CON (R¹) CH₂ COOM

wherein R is a C₉-C₁₇ linear or branched alkyl or alkenyl group, R¹ is a C₁-C₄ alkyl group and M is an alkali metal ion. Preferred examples are the lauroyl, Cocoyl (C₁₂-C₁₄), myristyl and oleyl methyl sarcosinates in the form of their sodium salts.

One class of nonionic surfactants useful in the present invention comprises condensates of ethylene oxide with a hydrophobic moiety, providing surfactants having an average hydrophilic-lipophilic balance (HLB) in the range from 8 to 17, preferably from 9.5 to 13.5, more preferably from 10 to 12.5. The hydrophobic (lipophilic) moiety may be aliphatic or aromatic in nature and the length of the polyoxyethylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Especially preferred nonionic surfactants of this type are the C₉-C₁₅ primary alcohol ethoxylates containing 3-8 moles of ethylene oxide per mole of alcohol, particularly the C₁₄-C₁₅ primary alcohols containing 6-8 moles of ethylene oxide per mole of alcohol and the C₁₂-C₁₄ primary alcohols containing 3-5 moles of ethylene oxide per mole of alcohol.

One particular class of adjunct nonionic surfactants especially useful herein comprises the polyhydroxy fatty acid amides of the formula:



wherein R¹ is H, C₁-C₈ hydrocarbyl, 2-hydroxyethyl, 2-hydroxypropyl, or a mixture thereof, preferably C₁-C₄ alkyl, more preferably C₁ or C₂ alkyl, most preferably C₁ alkyl (ie. methyl); and R² is a C₅-C₃₂ hydrocarbyl moiety, preferably straight chain C₇-C₁₉ alkyl or alkenyl, more preferably straight chain C₉-C₁₇ alkyl or alkenyl, most preferably straight chain C₁₁-C₁₉ alkyl or alkenyl, or a mixture thereof; and Z is a polyhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with at least 2 (in the case of glyceraldehyde) or at least 3 hydroxyls (in the case of other reducing sugars) directly connected to the chain, or an alkoxyated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl moiety. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose, as well as glyceraldehyde. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilised as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of

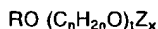
-CH₂-(CHOH)_n-CH₂OH, -CH(CH₂OH)-(CHOH)_n-CH₂OH, -CH₂-(CHOH)₂(CHOR¹)(CHOH)-CH₂OH, where n is an integer from 1 to 5, inclusive, and R¹ is H or a cyclic mono or polysaccharide, and alkoxyated derivatives thereof. Most preferred are glycityls wherein n is 4, particularly

-CH₂-(CHOH)₄-CH₂OH.

In Formula (I), R¹ can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-isobutyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl. For highest sudsing, R¹ is preferably methyl or hydroxyalkyl. If lower sudsing is desired R¹ is preferably C₂-C₈ alkyl, especially n-propyl, iso-propyl, n-butyl, iso-butyl, pentyl, hexyl and 2-ethyl hexyl.

R²-CO-N< can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

Another class of nonionic surfactants comprises alkyl polyglucoside compounds of general formula



wherein Z is a moiety derived from glucose; R is a saturated hydrophobic alkyl group that contains from 12 to 18 carbon atoms; t is from 0 to 10 and n is 2 or 3; x is from 1.3 to 4, the compounds including less than 10% unreacted fatty alcohol and less than 50% short chain alkyl polyglucosides. Compounds of this type and their use in detergent compositions are disclosed in EP-B 0070074, 0070077, 0075996 and 0094118.

A further class of surfactants are the semi-polar surfactants such as amine oxides. Suitable amine oxides are selected from mono C₈-C₂₀, preferably C₁₀-C₁₄ N-alkyl or alkenyl amine oxides and propylene-1,3-diamine dioxides wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

5 Cationic surfactants can also be used in the detergent compositions herein and suitable quaternary ammonium surfactants are selected from mono C₈-C₁₆, preferably C₁₀-C₁₄ N-alkyl or alkenyl ammonium surfactants wherein remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

The detergent compositions comprise from 5% to 20% of surfactant but more usually comprise from 7% to 20%, more preferably from 10% to 15% surfactant by weight of the compositions.

10 Combinations of surfactant types are preferred, more especially anionic-nonionic and also anionic-nonionic-cationic blends. Particularly preferred combinations are described in GB-A-2040987 and EP-A-0087914. Although the surfactants can be incorporated into the compositions as mixtures, it is preferable to control the point of addition of each surfactant in order to optimise the physical characteristics of the composition and avoid processing problems. Preferred modes and orders of surfactant addition are described hereinafter.

15 Another highly preferred component of detergent compositions incorporating the coated peroxy acid precursor particulates of the invention is a detergent builder system comprising one or more non-phosphate detergent builders. These can include, but are not restricted to alkali metal carbonates, bicarbonates, silicates, aluminosilicates, monomeric polycarboxylates, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more than two carbon atoms, organic phosphonates and aminoalkylene poly (alkylene phosphonates) and mixtures of any of the foregoing. The builder system is present in an amount of from 25% to 60% by weight of the composition, more preferably from 30% to 60% by weight.

25 Preferred builder systems are free of boron compounds and any polymeric organic materials are preferably biodegradable.

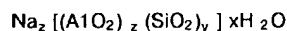
Suitable silicates are those having an SiO₂:Na₂O ratio in the range from 1.6 to 3.4, the so-called amorphous silicates of SiO₂ : Na₂O ratios from 2.0 to 2.8 being preferred. These materials can be added at various points of the manufacturing process, such as in a slurry of components that are spray dried or in the form of an aqueous solution serving as an agglomerating agent for other solid components, or, where the silicates are themselves in particulate form, as solids to the other particulate components of the composition.

30 Within the silicate class, highly preferred materials are crystalline layered sodium silicates of general formula



wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Crystalline layered sodium silicates of this type are disclosed in EP-A-0164514 and methods for their preparation are disclosed in DE-A-3417649 and DE-A-3742043. For the purposes of the present invention, x in the general formulae above has a value of 2, 3 or 4 and is preferably 2. More preferably M is sodium and y is 0 and preferred examples of this formula comprise the α and δ forms of Na₂Si₂O₅. These materials are available from Hoechst AG FRG as respectively NaSKS-11 and NaSKS-6. The most preferred material is δ - Na₂Si₂O₅, (NaSKS-6). Crystalline layered silicates are incorporated either as dry mixed solids, or as solid components of agglomerates with other components.

45 Whilst a range of aluminosilicate ion exchange materials can be used, preferred sodium aluminosilicate zeolites have the unit cell formula

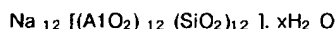


50 wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate materials are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

The above aluminosilicate ion exchange materials are further characterised by a particle size diameter of from 0.1 to 10 micrometers, preferably from 0.2 to 4 micrometers. The term "particle size diameter" herein represents the average particle size diameter of a given ion exchange material as determined by conventional analytical techniques such as, for example, microscopic determination utilizing a scanning electron microscope or by means of a laser granulometer. The aluminosilicate ion exchange materials are further characterised by their calcium ion exchange capacity, which is at least 200 mg equivalent of CaCO₃

water hardness/g of aluminosilicate, calculated on an anhydrous basis, and which generally is in the range of from 300 mg eq./g to 352 mg eq./g. The aluminosilicate ion exchange materials herein are still further characterised by their calcium ion exchange rate which is at least 130 mg equivalent of CaCO_3 /litre/minute/(g/litre) [2 grains Ca^{++} /gallon/minute/(gram/gallon)] of aluminosilicate (anhydrous basis), and which generally lies within the range of from 130 mg equivalent of CaCO_3 /litre/minute/(gram/litre) [2 grains/gallon/minute/(gram/gallon)] to 390 mg equivalent of CaCO_3 /litre/minute/(gram/litre) [6 grains/gallon/minute/(gram/gallon)], based on calcium ion hardness. Optimum aluminosilicates for builder purposes exhibit a calcium ion exchange rate of at least 260 mg equivalent of CaCO_3 /litre/minute/(gram/litre) [4 grains/gallon/minute/(gram/gallon)].

Aluminosilicate ion exchange materials useful in the practice of this invention are commercially available and can be naturally occurring materials, but are preferably synthetically derived. A method for producing aluminosilicate ion exchange materials is discussed in US Patent No. 3,985,669. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite B, Zeolite MAP (as disclosed in EP-A-0384070), Zeolite X, Zeolite HS and mixtures thereof. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material is Zeolite A and has the formula



wherein x is from 20 to 30, especially 27. Zeolite X of formula $\text{Na}_{86} [(\text{AlO}_2)_{86} (\text{SiO}_2)_{106}] \cdot 276 \text{H}_2 \text{O}$ is also suitable, as well as Zeolite HS of formula $\text{Na}_6 [(\text{AlO}_2)_6 (\text{SiO}_2)_6] \cdot 7.5 \text{H}_2 \text{O}$.

Suitable water-soluble monomeric or oligomeric carboxylate builders can be selected from a wide range of compounds but such compounds preferably have a first carboxyl logarithmic acidity/constant (pK_1) of less than 9, preferably of between 2 and 8.5, more preferably of between 4 and 7.5.

The logarithmic acidity constant is defined by reference to the equilibrium



where A is the fully ionized carboxylate anion of the builder salt.

The equilibrium constant is therefore

$$K_1 = \frac{(\text{H}^+ \text{A})}{(\text{H}^+) (\text{A})}$$

and $\text{pK}_1 = \log_{10} K_1$.

For the purposes of this specification, acidity constants are defined at 25 °C and at zero ionic strength.

Literature values are taken where possible (see Stability Constants of Metal-Ion Complexes, Special Publication No. 25, The Chemical Society, London): where doubt arises they are determined by potentiometric titration using a glass electrode.

Preferred carboxylates can also be defined in terms of their calcium ion stability constant ($\text{pK}_{\text{Ca}^{++}}$) defined, analogously to pK_1 , by the equations

$$\text{pK}_{\text{Ca}^{++}} = \log_{10} K_{\text{Ca}^{++}}$$

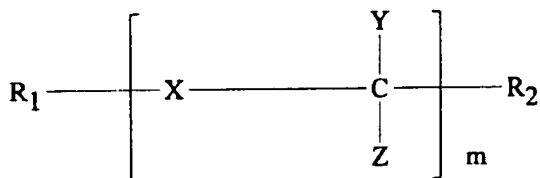
$$\text{where } K_{\text{Ca}^{++}} = \frac{(\text{Ca}^{++} \text{A})}{(\text{Ca}^{++}) (\text{A})}$$

Preferably, the polycarboxylate has a $\text{pK}_{\text{Ca}^{++}}$ in the range from about 2 to about 7 especially from about 3 to about 6. Once again literature values of stability constant are taken where possible. The stability constant is defined at 25 °C and at zero ionic strength using a glass electrode method of measurement as described in Complexation in Analytical Chemistry by Anders Ringbom (1963).

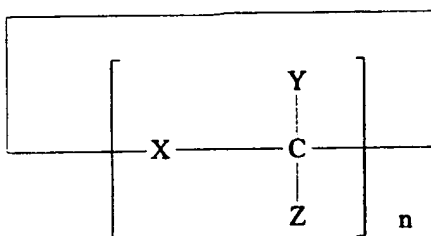
The carboxylate or polycarboxylate builder can be monomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

Monomeric and oligomeric builders can be selected from acyclic, alicyclic, heterocyclic and aromatic carboxylates having the general formulae

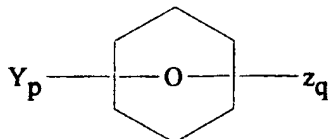
(a)



(b)



or
(c)



wherein R_1 represents $\text{H}, \text{C}_{1-30}$ alkyl or alkenyl optionally substituted by hydroxy, carboxy, sulfo or phosphono groups or attached to a polyethylenoxy moiety containing up to 20 ethyleneoxy groups; R_2 represents H, C_{1-4} alkyl, alkenyl or hydroxy alkyl, or alkaryl, sulfo, or phosphono groups;

X represents a single bond; O; S; SO ; SO_2 ; or NR_1 ;

Y represents H; carboxy; hydroxy; carboxymethoxy; or

C_{1-30} alkyl or alkenyl optionally substituted by hydroxy or carboxy groups;

Z represents H; or carboxy;

m is an integer from 1 to 10;

n is an integer from 3 to 6;

p, q are integers from 0 to 6, $p + q$ being from 1 to 6; and wherein, X, Y, and Z each have the same or different representations when repeated in a given molecular formula, and wherein at least one Y or Z in a molecule contain a carboxyl group.

Suitable carboxylates containing one carboxy group include lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831,368, 821,369 and 821,370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offenlegenschrift 2,446,686, and 2,446,687 and U.S. Patent No. 3,935,257 and the sulfinyl carboxylates described in Belgian Patent No. 840,623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as

succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydrofuran - cis, cis, cis-tetracarboxylates, 2,5-tetrahydrofuran - cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane - hexacarboxylates and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343. Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as components of builder systems of detergent compositions in accordance with the present invention.

Suitable water soluble chelant salts include the homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MWt 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 70,000, especially about 40,000.

These materials are normally used at levels of from 0.5% to 10% by weight more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

Salts of aspartic and glutamic acid homo and copolymers are also suitable polycarboxylate chelants and are disclosed in WO93/06202 and EP-A-0454126.

Further classes of chelant salt comprise the organic phosphonates and amino alkylene poly (alkylene phosphonates) which include alkali metal ethane 1-hydroxy diphosphonates, nitrilo trimethylene phosphonates, ethylene diamine tetra methylene phosphonates and diethylene triamine penta methylene phosphonates, although these materials are less preferred where the minimisation of phosphorus compounds in the compositions is desired.

Preferred biodegradable, non-phosphorous chelants include ethylenediamine disuccinate ("EDDS"; see USP 4,704,233, Hartman and Perkins), ethylenediamine-N,N'-diglutamate (EDDG) and 2-hydroxypropylenediamine-N,N'-disuccinate (HPDDS) compounds.

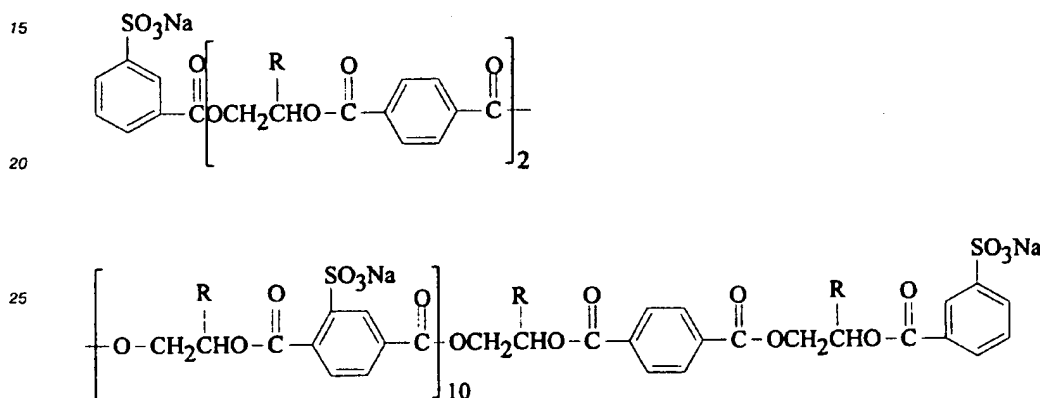
For the purposes of detergent compositions embodying the surface treated bleach precursor particulates of the invention, the non-phosphate builder ingredient will comprise from 25% to 60% by weight of the compositions, more preferably from 30% to 60% by weight. Within the preferred compositions, sodium aluminosilicate such as Zeolite A will comprise from 20% to 60% by weight of the total amount of builder, a monomeric or oligomeric carboxylate will comprise from 10% to 30% by weight of the total amount of builder and a crystalline layered silicate will comprise from 10% to 65% by weight of the total amount of builder. In such compositions the builder ingredient preferably also incorporates a combination of auxiliary inorganic and organic builders such as sodium carbonate and maleic anhydride/acrylic acid copolymers in amounts of up to 35% by weight of the total builder.

Anti-redeposition and soil-suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, vinyl pyrrolidone polymers of MWt 5000 - 40000 and homo-or co-polymeric polycarboxylic acids or their salts. Polymers of the latter type include copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. These materials are normally used at levels of from 0.5% to 10% by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

Other useful polymeric materials are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000. These are used at levels of from 0.20% to 5% more preferably from 0.25% to 2.5% by weight. These polymers and the previously mentioned homo- or co-polymeric polycarboxylate salts are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

Preferred optical brighteners are anionic in character, examples of which are disodium 4,4'-bis-(2-diethanolamino-4-anilino -s- triazin-6-ylamino)stilbene-2:2' disulphonate, disodium 4,4'-bis-(2-morpholino -4-anilino-2-triazin-6-ylaminostilbene-2:2'-disulphonate, disodium 4,4'-bis-(2,4-dianilino-s-triazin-6-ylamino)-stilbene-2:2' - disulphonate, monosodium 4',4''-bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2-sulphonate, disodium 4,4'-bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-2-triazin-6-ylamino)stilbene-2,2' - disulphonate, disodium 4,4'-bis-(4-phenyl-2,1,3-triazol-2-yl)stilbene-2,2' disulphonate, disodium 4,4'-bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2'disulphonate and sodium 2(stilbyl-4''-(naphtho-1',2':4,5)-1,2,3 - triazole-2''- sulphonate and disodium 4,4'-bis{(4-anilino-6'morpholino-1,3,5-triazin-2-yl) amino) stilbene-2,2' disulfonate.

Soil-release agents useful in compositions of the present invention are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol units in various arrangements. Examples of such polymers are disclosed in the commonly assigned US Patent Nos. 4116885 and 4711730 and European Published Patent Application No. 0272033. A particularly preferred polymer has the formula



Certain polymeric materials such as the previously-described polyvinyl pyrrolidones of MWt 5000-40000, preferably 10000-15000, also form useful agents in preventing the transfer of labile dyestuffs between fabrics during the washing process.

Another optional detergent composition ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms, exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent-impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

As mentioned above, useful silicone suds controlling agents can comprise a mixture of an alkylated siloxane, of the type referred to hereinbefore, and solid silica. Such mixtures are prepared by affixing the silicone to the surface of the solid silica. A preferred silicone suds controlling agent is represented by a hydrophobic silanated (most preferably trimethylsilanated) silica having a particle size in the range from 10 nanometers to 20 nanometers and a specific surface area above 50 m²/g, intimately admixed with dimethyl silicone fluid having a molecular weight in the range from about 500 to about 200,000 at a weight ratio of silicone to silanated silica of from about 1:1 to about 1:2.

A preferred silicone suds controlling agent is disclosed in Bartollota et al. US Patent 3,933,672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2,646,126 published April 28, 1977. An example of such a compound is DC0544, commercially available from Dow Corning, which is a siloxane/glycol copolymer.

The suds suppressors described above are normally employed at levels of from 0.001% to 0.5% by weight of the composition, preferably from 0.01% to 0.1% by weight.

The preferred methods of incorporation comprise either application of the suds suppressors in liquid form by spray-on to one or more of the major components of the composition or alternatively the formation of the suds suppressors into separate particulates that can then be mixed with the other solid components of the composition. The incorporation of the suds modifiers as separate particulates also permits the inclusion therein of other suds controlling materials such as C₂₀-C₂₄ fatty acids, microcrystalline waxes and

high MWt copolymers of ethylene oxide and propylene oxide which would otherwise adversely affect the dispersibility of the matrix. Techniques for forming such suds modifying particulates are disclosed in the previously mentioned Bartolotta et al US Patent No. 3,933,672.

Another optional ingredient useful in the present invention is one or more enzymes.

Preferred enzymatic materials include the commercially available amylases, neutral and alkaline proteases, lipases, peroxidases, esterases and cellulases conventionally incorporated into detergent compositions. Suitable proteolytic enzymes are described in GB-A-1243784, EP-A-0130756 and USP 5185250 and 5204015. Suitable amylases are disclosed in GB-A-1296839 while cellulases are disclosed in USP 4435307, GB-A-2075028 and 2095275. Lipases for use in detergent compositions are disclosed in GB-A-1372034 and EP-A-0341947. A suitable peroxidase is disclosed by WO89/099813. A wide range of enzyme materials and means for their incorporation into synthetic detergent granules is also discussed in US Patents 3,519,570 and 3,533,139.

Fabric softening agents can also be incorporated into detergent compositions in accordance with the present invention. These agents may be inorganic or organic in type. Inorganic softening agents are exemplified by the smectite clays disclosed in GB-A-1,400,898. Organic fabric softening agents include the water insoluble tertiary amines as disclosed in GB-A-1514276 and EP-B-0011340.

Their combination with mono C₁₂-C₁₄ quaternary ammonium salts is disclosed in EP-B-0026527 & 528. Other useful organic fabric softening agents are the dilong chain amides as disclosed in EP-B-0242919. Additional organic ingredients of fabric softening systems include high molecular weight polyethylene oxide materials as disclosed in EP-A-0299575 and 0313146.

Levels of smectite clay are normally in the range from 5% to 15%, more preferably from 8% to 12% by weight, with the material being added as a dry mixed component to the remainder of the formulation. Organic fabric softening agents such as the water-insoluble tertiary amines or dilong chain amide materials are incorporated at levels of from 0.5% to 5% by weight, normally from 1% to 3% by weight, whilst the high molecular weight polyethylene oxide materials and the water soluble cationic materials are added at levels of from 0.1% to 2%, normally from 0.15% to 1.5% by weight. Where a portion of the composition is spray dried, these materials can be added to the aqueous slurry fed to the spray drying tower, although in some instances it may be more convenient to add them as a dry mixed particulate, or spray them as a molten liquid on to other solid components of the composition.

The surface treated peroxyacid bleach precursor particulates of the present invention are particularly useful in concentrated granular detergent compositions that are characterised by a relatively high density in comparison with conventional laundry detergent compositions. Such high density compositions have a bulk density of at least 650 g/litre, more usually at least 700 g/litre and more preferably in excess of 800 g/litre.

Bulk density is measured by means of a simple funnel and cup device consisting of a conical funnel moulded rigidly on a base and provided with a flap valve at its lower extremity to allow the contents of the funnel to be emptied into an axially aligned cylindrical cup disposed below the funnel. The funnel is 130 mm and 40 mm at its respective upper and lower extremities. It is mounted so that the lower extremity is 140 mm above the upper surface of the base. The cup has an overall height of 90 mm, an internal height of 87 mm and an internal diameter of 84 mm. Its nominal volume is 500 ml.

To carry out a measurement, the funnel is filled with powder by hand pouring, the flap valve is opened and powder allowed to overfill the cup. The filled cup is removed from the frame and excess powder removed from the cup by passing a straight edged implement e.g. a knife, across its upper edge. The filled cup is then weighed and the value obtained for the weight of powder doubled to provide the bulk density in g/litre. Replicate measurements are made as required.

Concentrated detergent compositions also normally incorporate at least one multi-ingredient component i.e. they do not comprise compositions formed merely by dry-mixing individual ingredients. Compositions in which each individual ingredient is dry-mixed are generally dusty, slow to dissolve and also tend to cake and develop poor particle flow characteristics in storage.

Subject to the above bulk density and component content limitations, the detergent compositions of the invention can be made via a variety of methods including dry mixing, spray drying, agglomeration and granulation and preferred methods involve combinations of these techniques. A preferred method of making the compositions involves a combination of spray drying, agglomeration in a high speed mixer and dry mixing.

Preferred detergent compositions in accordance with the invention comprise at least two particulate multi-ingredient components. Such detergent compositions conventionally contain a mixture of surfactants. In a first embodiment, surfactants having a low rate of dissolution are contained in a separate granular component to those surfactants having a high rate of dissolution. In a second embodiment, the surfactants are separated by type, with anionic surfactants in one component and nonionic surfactants in another

component.

In the first such embodiment, in which the dissolution rate of the surfactant is determinative, the first component comprises at least 15%, conventionally from 25% to 50%, but more preferably no more than 35% by weight of the composition and the second component from 1% to 50%, more preferably 10% to 40% by weight of the composition.

The first component comprises a particulate incorporating an anionic surfactant in an amount of from 0.75% to 40% by weight of the powder and one or more inorganic and/or organic salts in an amount of from 99.25% to 60% by weight of the powder. The particulate can have any suitable form such as granules, flakes, prills, marumes or noodles but is preferably granular. The granules themselves may be agglomerates formed by pan or drum agglomeration or by in-line mixers but can also be spray dried particles produced by atomising an aqueous slurry of the ingredients in a hot air stream which removes most of the water. These spray dried granules are then subjected to densification steps, e.g. by high speed cutter mixers and/or compacting mills, to increase density before being reagglomerated. For illustrative purposes, the first component is described hereinafter as a spray dried powder.

Suitable anionic surfactants for the purposes of the first component comprise slowly dissolving linear alkyl sulfate salts in which the alkyl group has an average of from 16 to 22 carbon atoms, and linear alkyl carboxylate salts in which the alkyl group has an average of from 16 to 24 carbon atoms. The alkyl groups for both types of surfactant are preferably derived from natural sources such as tallow fat and marine oils.

The level of anionic surfactant in the spray dried powder forming the first component is from 0.75% to 40% by weight, more usually 2.5% to 25% preferably from 3% to 20% and most preferably from 5% to 15% by weight. Water-soluble surfactants such as linear alkyl benzene sulphonates or C₁₄-C₁₅ alkyl sulphates can be included or alternatively may be applied subsequently to the spray dried powder by spray on.

The other major ingredient of the spray dried powder is one or more inorganic or organic salts that provide the crystalline structure for the granules. The inorganic and/or organic salts may be water-soluble or water-insoluble, the latter type being comprised by the, or the major part of the, water-insoluble builders where these form part of the builder ingredient. Suitable water soluble inorganic salts include the alkali metal carbonates and bicarbonates. Alkali metal silicates other than crystalline layered silicates can also be present in the spray dried granule provided that aluminosilicate does not form part of the spray dried component.

However, in concentrated detergent compositions it is preferred that water-soluble sulphate, particularly sodium sulphate, should not be present at a level of more than 2.5% by weight of the composition. Preferably no sodium sulphate is added as a separate ingredient and its incorporation as a by-product e.g. with sulph(on)ated surfactants, should be minimised.

Where an aluminosilicate zeolite forms the, or part of the, builder ingredient, it is preferred that it is not added directly by dry-mixing to the other components, but is incorporated into the multi-ingredient component(s). Where incorporation of the zeolite takes place in the spray-dried granule, the latter should not include high levels of silicate in order to avoid the formation of insoluble materials under the high temperature conditions of the crutcher. In such circumstances, incorporation of the silicate can be achieved in several ways, e.g. by producing a separate silicate-containing spray-dried particulate, by incorporating the silicate into an agglomerate of other ingredients, or more preferably by adding the silicate as a dry mixed solid ingredient.

The first component can also include up to 15% by weight of miscellaneous ingredients such as brighteners, anti-redeposition agents, photoactivated bleaches (such as tetrasulfonated zinc phthalocyanine) and heavy metal sequestering agents. Where the first component is a spray dried powder it will normally be dried to a moisture content of from 7% to 11% by weight, more preferably from 8% to 10% by weight of the spray dried powder. Moisture contents of powders produced by other processes such as agglomeration may be lower and can be in the range 1-10% by weight.

The particle size of the first component is conventional and preferably not more than 5% by weight should be above 1.4mm, while not more than 10% by weight should be less than 0.15 mm in maximum dimension. Preferably at least 60%, and most preferably at least 80%, by weight of the powder lies between 0.7 mm and 0.25 mm in size. For spray dried powders, the bulk density of the particles from the spray drying tower is conventionally in the range from 540 to 600 g/litre and this is then enhanced by further processing steps such as size reduction in a high speed cutter/mixer followed by compaction. Alternatively, processes other than spray drying may be used to form a high density particulate directly.

In a particularly preferred process for making detergent compositions incorporating the coated peroxyacid bleach precursor particulates of the invention, part of the spray dried product comprising the first granular component is diverted and subjected to a low level of nonionic surfactant spray on before being

reblended with the remainder.

A second component of a preferred detergent composition is another multi-ingredient particulate containing a water soluble surfactant.

This may be anionic, nonionic, cationic or semipolar in type or a mixture of any of these. Suitable surfactants are listed hereinbefore but preferred surfactants are C₁₄-C₁₅ alkyl sulphates, linear C₁₁-C₁₅ alkyl benzene sulphonates and fatty C₁₄-C₁₈ methyl ester sulphonates.

The second component may have any suitable physical form, i.e. it may take the form of flakes, prills, marumes, noodles, ribbons, or granules which may be spray-dried or non spray-dried agglomerates. Although the second component could in theory comprise the water soluble surfactant on its own, in practice at least one organic or inorganic salt is included to facilitate processing. This provides a degree of crystallinity, and hence acceptable flow characteristics, to the particulate and may be any one or more of the organic or inorganic salts present in the first component.

The particle size range of the second component should be such as to obviate segregation from the particles of the first component when blended therewith. Thus not more than 5% by weight should be above 1.4 mm while not more than 10% should be less than 0.15 mm in maximum dimension.

The bulk density of the second component will be a function of its mode of preparation. However, the preferred form of the second component is a mechanically mixed agglomerate which may be made by adding the ingredients dry or with an agglomerating agent to a pan agglomerator, Z blade mixer or more preferably an in-line mixer such as those manufactured by Schugi (Holland) BV, 29 Chroomstraat 8211 AS, Lelystad, Netherlands and Gebruder Lodige Maschinenbau GmbH, D-4790 Paderborn 1, Elsenerstrasse 7-9, Postfach 2050 F.R.G. By this means the second component can be given a bulk density in the range from 650 g/litre to 1190 g/litre more preferably from 750 g/litre to 850 g/litre.

Preferred compositions include a level of alkali metal carbonate in the second component corresponding to an amount of from 3% to 15% by weight of the composition, more preferably from 5% to 12% by weight. This will provide a level of carbonate in the second component of from 20% to 40% by weight.

A highly preferred ingredient of the second component is also a hydrated water insoluble aluminosilicate ion exchange material of the synthetic zeolite type, described hereinbefore, present at from 10% to 35% by weight of the second component. The amount of water insoluble aluminosilicate material incorporated in this way is from 1% to 10% by weight of the composition, more preferably from 2% to 8% by weight.

In one process for preparing the second component, the surfactant salt is formed in situ in an inline mixer. The liquid acid form of the surfactant is added to a mixture of particulate anhydrous sodium carbonate and hydrated sodium aluminosilicate in a continuous high speed blender, such as a Lodige KM mixer, and neutralised to form the surfactant salt whilst maintaining the particulate nature of the mixture. The resultant agglomerated mixture forms the second component which is then added to other components of the product. In a variant of this process, the surfactant salt is pre-neutralised and added as a viscous paste to the mixture of the other ingredients. In the variant, the mixer serves merely to agglomerate the ingredients to form the second component.

In a second embodiment of the detergent composition aspect of the invention, the first component contains all of the anionic surfactants while the second component contains all of the nonionic surfactants. In this embodiment the anionic surfactant-containing component can be made by spray drying as previously described, but is preferably made by an agglomeration technique or by in line mixing and extrusion as described hereinbefore for the second component. The nonionic surfactant containing component is made by agglomeration or by in line mixing and extrusion as described before. For both components, inorganic salts such as sodium carbonate and/or hydrated sodium aluminosilicate are added to the mixture in order to provide particles of acceptable granulometry and flow characteristics, in a manner not forming part of the present invention and well known to the skilled person. One or both components may also be provided with a dust coating of zeolite or similar material to further enhance their flow characteristics.

The first and second components together with the coated bleach precursor particulate and the perhydrate bleach, other dry mix ingredients such as any carboxylate chelating agent, soil-release polymer, silicate of conventional or crystalline layered type, and enzyme are then fed to a conveyor belt, from which they are transferred to a horizontally rotating drum in which perfume and silicone suds suppressor are sprayed on to the product. In highly preferred compositions, a further drum mixing step is employed in which a low (approx. 2% by weight) level of finely divided crystalline material is introduced to increase density and improve granular flow characteristics.

In preferred concentrated detergent products incorporating an alkali metal percarbonate as the perhydrate salt it has been found necessary to control several aspects of the product such as its heavy metal ion content and its equilibrium relative humidity. Sodium percarbonate-containing compositions of this type

having enhanced stability are disclosed in the commonly assigned International Application Publication No. WO92/06163.

Compositions in accordance with the invention can also benefit from delivery systems that provide transient localised high concentrations of product in the drum of an automatic washing machine at the start of the wash cycle, thereby also avoiding problems associated with loss of product in the pipework or sump of the machine.

Delivery to the drum can most easily be achieved by incorporation of the composition in a bag or container from which it is rapidly releasable at the start of the wash cycle in response to agitation, a rise in temperature or immersion in the wash water in the drum. Alternatively the washing machine itself may be adapted to permit direct addition of the composition to the drum e.g. by a dispensing arrangement in the access door.

Products comprising a detergent composition enclosed in a bag or container are usually designed in such a way that container integrity is maintained in the dry state to prevent egress of the contents when dry, but are adapted for release of the container contents on exposure to a washing environment, normally on immersion in an aqueous solution.

Usually the container will be flexible, such as a bag or sachet, an exemplary sachet being disclosed in the commonly assigned European Patent Application No. 0345838. The bag may be of fibrous construction coated with a water impermeable protective material so as to retain the contents, such as is disclosed in European published Patent Application No. 0018678. Alternatively it may be formed of a water-insoluble synthetic polymeric material provided with an edge seal or closure designed to rupture in aqueous media as disclosed in European published Patent Application Nos. 0011500, 0011501, 0011502, and 0011968. A convenient form of water frangible closure comprises a water soluble adhesive disposed along and sealing one edge of a pouch formed of a water impermeable polymeric film such as polyethylene or polypropylene.

In a variant of the bag or container form, laminated sheet products can be employed in which a central flexible layer is impregnated and/or coated with a composition and then one or more outer layers are applied to produce a fabric-like aesthetic effect. The layers may be sealed together so as to remain attached during use or may separate on contact with water to facilitate the release of the coated or impregnated material.

An alternative laminate form comprises one layer embossed or deformed to provide a series of pouch-like containers into each of which the detergent components are deposited in measured amounts, with a second layer overlying the first layer and sealed thereto in those areas between the pouch-like containers where the two layers are in contact. The components may be deposited in particulate, paste or molten form and the laminate layers should prevent egress of the contents of the pouch-like containers prior to their addition to water. The layers may separate or may remain attached together on contact with water, the only requirement being that the structure should permit rapid release of the contents of the pouch-like containers into solution. The number of pouch-like containers per unit area of substrate is a matter of choice but will normally vary between 500 and 25,000 per square metre.

Suitable materials which can be used for the flexible laminate layers in this aspect of the invention include, among others, sponges, paper and woven and non-woven fabrics.

However the preferred means of carrying out a wash process using a detergent composition in accordance with the invention is to introduce the composition into the liquid surrounding the fabrics that are in the drum via a reusable dispensing device having walls that are permeable to liquid but impermeable to the composition.

Devices of this kind are disclosed in European Patent Application Publication Nos. 0290332, 0343069 & 0343070. The latter Application discloses a device comprising a flexible sheath in the form of a bag extending from a support ring defining an orifice, the orifice being adapted to admit to the bag sufficient product for one washing cycle in a washing cycle. A portion of the washing medium flows through the orifice into the bag, dissolves the product, and the solution then passes outwardly through the orifice into the washing medium. The support ring is provided with a masking arrangement to prevent egress of wetted, undissolved, product, this arrangement typically comprising radially extending walls extending from a central boss in a spoked wheel configuration, or a similar structure in which the walls have a helical form.

The invention is illustrated in the following non limiting Examples, in which all percentages are on a weight basis unless otherwise stated.

In the detergent composition aspect of the invention, the abbreviated component identifications have the following meanings:

C ₁₂ LAS	: Sodium linear C ₁₂ alkyl benzene sulphonate
CnAS	: Sodium coconut alkyl sulphate
TAS	: Sodium tallow alcohol sulphate

	C45AS	: Sodium C ₁₂ -C ₁₅ linear alkyl sulphate
	CC ₂₅ E ₃ S	: Sodium C ₁₂ -C ₁₅ branched alkyl sulphate condensed with three moles of ethylene oxide
5	Soap	: Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and a coconut oils.
	C45E7	: A C ₁₄ - ₁₅ predominantly linear primary alcohol condensed with an average of 7 moles of ethylene oxide
	CD5 E3	: A C ₁₂ - ₁₅ branched primary alcohol condensed with an average of 3 moles of ethylene oxide
10	25E5	: A C ₁₂ - ₁₅ branched primary alcohol condensed with an average of 5 moles of ethylene oxide
	Glucamide	: C ₁₂ -C ₁₄ methyl glucamide
	Polyethylene Glycol	: Homopolymer of ethylene glycol of MWt 4000
	Silicate	: Amorphous Sodium Silicate (SiO ₂ :Na ₂ O ratio normally follows)
15	NaSKS-6	: Crystalline layered silicate of formula δ -Na ₂ Si ₂ O ₅
	Carbonate	: Anhydrous sodium carbonate
	Bicarbonate	: Anhydrous sodium bicarbonate
	MgSO ₄	: Anhydrous magnesium sulphate
	Sulphate	: Anhydrous sodium sulphate
20	Zeolite A	: Hydrated Sodium Aluminosilicate of formula Na ₁₂ (Al ₁₀ SiO ₂) ₁₂ . 27H ₂ O having a primary particle size in the range from 1 to 10 micrometers
	STPP	: Anhydrous sodium tripolyphosphate
	Citrate	: Tri-sodium citrate dihydrate
	Citric Acid	: Anhydrous citric acid
25	Polyacrylate	: Homopolymer of acrylic acid of MWt 4000
	MA/AA	: Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000.
	Perborate	: Sodium perborate tetrahydrate of nominal formula NaBO ₂ .3H ₂ O.H ₂ O ₂
	Perborate Monohydrate	: Anhydrous sodium perborate bleach of nominal formula NaBO ₂ .H ₂ O ₂
30	Percarbonate	: Sodium Percarbonate of nominal formula 2Na ₂ CO ₃ .3H ₂ O ₂
	CMC	: Sodium carboxymethyl cellulose
	Fluorescer	: Disodium 4,4'-bis(4-anilino-6--morpholino-1.3.5-triazin-2-yl)amino) stilbene-2:2'-disulphonate.
	DETPMP	: Diethylene triamine penta (Methylene phosphonic acid), marketed by Monsanto under the Trade name Dequest 2060
35	EDDS :	: S,S ethylene diamine disuccinate
	Mixed Suds	: 25% paraffin wax Mpt 50 °C, 17%
	Suppressor	: hydrophobic silica, 58% paraffin oil.
	Savinase	: proteolytic enzyme activity 4KNPU/g
40	Alcalase 3T	: proteolytic enzyme activity 3AU/g
	Cellulase IT	: cellulytic enzyme activity 1000 SCEVU/g
	Termamyl 60T	: Amyloytic enzyme activity 60KNU/g
	Lipalase	: Lipolytic enzyme activity 100kLU/g
		all sold by NOVO Industries AS
45	S.R.P.	: Soil Release polymer of formula shown on page 33
	PVP	: polyvinylpyrrolidone of MWt 13000
	PVNP	: poly (4-vinyl pyridine)-N-oxide copolymer of vinyl imidazole and vinylpyrrolidone

Example 1

A coated agglomerate having the following formulation was made in an Eirich mixer (model RV02).

Benzoyl Caprolactam	2.60 kg (particle size <100 micrometers)
Anhydrous Citric acid	0.80 kg (median particle size approximately 50 micrometers)
Poly Ethylene Glycol 4000	0.60 kg
Anhydrous Citric acid	0.30 kg (median particle size approximately 50 micrometers)

The benzoyl caprolactam and Citric acid were added to the Eirich mixer and pre-mixed. The temperature of the powders was 24 °C. The molten nonionic binder, which was at a temperature of 55 °C, was added to this powder mix over a period of 35 seconds with the Eirich blades and drum rotating. The resulting preparation was mixed for a further 90 seconds. The temperature of the agglomerated particles was 31 °C and this temperature was maintained while the further 300g of anhydrous Citric acid was added over a period of 20 seconds to provide a powder coating of the agglomerate. The mixing was then stopped and the coated agglomerate product removed from the Eirich mixer and cooled to ambient temperature (15-20 °C).

This product was then sieved and materials that were greater than 1180 micrometers (2%) and smaller than 250 micrometers (6%) were removed.

The Coating Index (CI) of this material was found to be 0.25 using the lithium citrate analytical technique described hereinbefore.

Example 2

A coated agglomerate having the following formulation was made in an Eirich mixer (model RVO2).

Benzoyl Caprolactam	2.80 kg (particle size <100 micrometers)
MA/AA of MWt 60,000	0.40 kg (median particle size approximately 60 micrometers)
Poly Ethylene Glycol 4000	0.60 kg
Ma/AA* of MWt 60,000	0.20 kg (median particle size approximately 60 micrometers) as powder coating

*supplied as Sokolan 45 ex BASF

The Benzoyl Caprolactam and Sokolan CP45 were added to the Eirich mixer and pre-mixed. The temperature of the powders was 22 °C. The molten binder, which was at a temperature of 58 °C, was added to the powder mix, with the Eirich blades and pan rotating, over a period of 40 seconds. The resulting mass was further mixed for 90 seconds. The temperature of the agglomerated particles was 30 °C and this temperature was maintained while a further 200g of Sokolan CP45 was added over a period of 20 seconds to provide a powder coating to the agglomerate. The mixing was then stopped and the coated agglomerate product removed from the Eirich mixer and cooled to ambient temperature (15-20 °C).

The product was then sieved and materials that were greater than 1180 micrometers and smaller than 250 micrometers were removed.

The Coating Index of this material was found to be 0.32.

Example 3

A coated agglomerate of the following formulation was made in Eirich Mixer (Model RVO2)

	wt%
Benzoyl caprolactam	70
Zeolite A (median particle size 4-5 μ m)	6
PEG 4000	10
anhydrous Citric Acid (median particle size 60 μ m)	14
	<u>100</u>

n-benzoyl caprolactam was melted and fed a temperature of 79 °C to a Chill flaker (Simon Drum Flaker 20 cm diameter 30 cm width) having a coolant feed temperature of 44 °C to provide flakes with a thickness of less than 300 μ m. The benzoyl caprolactam flakes, citric acid and Zeolite A were fed to the rotating Eirich Mixer after which the molten polyethylene glycol, at a temperature of 58 °C, was added over a period of 40 seconds.

The amounts of added citric acid and Zeolite were such as to provide respectively, levels of 10% and 4% by weight of the mix. Mixing continued for a further 90 seconds to form agglomerates of the components, the temperature of the mass being approximately 30 °C. Powdered Citric acid and Zeolite A were then added to the agglomerates, and the mixing was continued for a further 20 seconds, to provide powder coating levels of approximately 2% Zeolite and 4% citric acid. The coated particles were cooled to a temperature of 20 °C in a fluid bed cooler before material of particle size >1180 μ m and <250 μ m was removed by sieving. The Powder Coating Index of the citric acid coating was found to be 0.28.

Example 4

The following detergent compositions are in accordance with the invention.

	A	B	C	D
C ₁₂ LAS	6.5	6.5	7.6	6.9
TAS	3.0	3.0	1.3	2.0
C ₂₅ E ₃ S	0.15	0.15	0.15	0.15
C ₄₅ E ₇	4.0	5.0	1.3	4.0
Zeolite	18.0	17.0	17.0	20
Citrate	-	-	1.5	5.5
Citric Acid	2.3	1.8	2.6	-
NaSKS-6	8.7	6.5	9.5	-
Carbonate	16.0	15.5	7.0	15.4
Silicate (2.0 ratio)	0.5	0.5	0.5	3.0
Bicarbonate	4.5	7.5	1.5	-
MA/AA Copolymer	4.0	4.5	3.2	4.0
CMC	0.3	0.3	0.2	0.3
Savinase	0.4	-	0.4	1.4
Lipolase	0.2	0.1	0.1	0.3
Cellulase 1T	0.15	0.15	-	0.1
Alcalase 3T	-	0.3	-	-
Perborate	-	-	9.0	11.6
Perborate Monohydrate	-	-	5.0	8.7
Percarbonate	17.5	16.5	-	-
DETPMP	0.4	0.4	0.4	0.4
MgSO ₄	0.4	0.4	0.4	0.4
Fluorescer	0.19	0.19	0.15	0.19
Suds Suppressor	0.8	0.8	0.8	0.8
Perfume	0.35	0.4	0.35	0.4
Detergent				
Additive composition	4.5 ⁽¹⁾	2.5 ⁽¹⁾	3.4 ⁽²⁾	5.0 ⁽¹⁾
Sulphate				
Minors etc. to	100	100	100	100

* (1) as in Example 1

(2) as in Example 2

A separate spray dried granular component is produced that incorporated a small quantity (0.3%) of the TAS, the MA/AA polymer, CMC, fluorescer chelant, magnesium sulphate and soil zeolite.

Compositions A-D are made in several stages. Firstly an anionic surfactant agglomerate is produced by combining the LAS, C₂₅E₃S, and most of the TAS together with the carbonate and most of the zeolite in an in-line mixer and this component, together with the particulate copolymer, is mixed with the surfactant agglomerate. The nonionic surfactant and optionally the suds suppressor component is then sprayed on to this mixture. Finally the remaining components are then added viz enzymes, and optionally the suds suppressor component, as prills or granules, citrate, bicarbonate and citric acid-SKS-6 agglomerate (where present), inorganic perhydrate bleach and coated bleach precursor (detergent additive) particles.

Finally perfume is sprayed on and a low level of zeolite is added as a dust coating. These products have a bulk density of at least 700g/litre.

Example 5

The following detergent compositions are in accordance with the invention

5		E	F	G	H	I	J	K	L	M
	TAS	-	-	-	-	-	2.0	-	-	2.4
10	CnTAS	-	9	9	-	-	-	-	-	-
	C₄₅AS	6.9	-	-	9	7.0	-	-	7.0	-
	C₂₅E₃S	1.7	-	-	-	-	-	-	-	-
15	C₁₂LAS	-	-	-	-	9.0	4.0	6.0	16.0	5.6
	C₄₅E₇	-	-	-	-	1.0	2.5	2.5	1.0	5.0
	C₂₅E₅	2.2	7	7	-	-	-	-	-	-
	C₂₅E₃	1.1	-	-	7	-	2.5	2.5	-	-
20	Glucamide	1.5	-	-	-	-	-	-	-	0.8
	Soap	-	-	-	-	-	1.0	1.0	2.0	-
	Zeolite A	10	22	22	30	22.0	-	24.0	6.0	-
25	STPP	-	-	-	-	-	24.0	-	-	21.2
	Citrate	-	2	-	2	-	-	-	-	-
	Citric Acid	2.5	-	-	-	-	-	-	-	-
30	NASKS-6	9.0	-	10	-	-	-	-	-	-
	Carbonate	7.0	13	6	13	16.0	6.0	13.0	20.0	7.0
	Silicate	-	3	-	3	1.0	7.0	3.0	5.0	8.0
	(2.0r)									
35	Sulphate	-	-	-	-	16.0	12.0	9.0	7.0	21.0
	MA/AA	3.3	3	4	3	3.0	2.0	4.0	6.0	1.8
	CMC	0.3	0.3	0.3	0.3	-	1.0	1.0	0	0.3
40	SRP	0.2	-	-	-	-	-	-	-	0.15
	PVP	-	-	0.5	-	0.5	-	-	0.5	-
	PVNO	0.02	-	-	-	-	-	-	-	-
	PEG 2000	-	-	-	-	-	-	-	-	0.3
45	Savinase	0.4	2	2	2	1.0	1.0	1.0	1.0	1.0
	Cellulase IT	0.11	-	-	-	-	-	-	-	0.10
	Lipalase	0.11	0.3	0.2	0.3	0.4	0.4	0.4	0.4	0.15
50	Termamyl									
	60T	0.8	-	-	-	-	-	-	-	-
	Pb4	-	-	-	-	-	18.0	18.0	-	13.0
55	Pb1	-	-	-	-	5.0	4.0	4.0	6.0	2.0
	PC	16	18	24	18	-	-	-	-	-

	E	F	G	H	I	J	K	L	M
Detergent Additive Composition	4.0 ⁽³⁾	3.5 ⁽²⁾	4.5 ⁽¹⁾	5.0 ⁽²⁾	6.0 ⁽¹⁾	3.0 ⁽¹⁾	3.0 ⁽²⁾	4.5 ⁽²⁾	2.0 ⁽²⁾
M₂SO₄	0.4	-	-	-	-	-	-	-	0.4
DETPMP	-	0.5	0.3	0.5	0.4	0.4	0.4	0.4	0.3
EDDS	0.2	-	-	-	-	-	-	-	-
Suds Suppressor	2.75	2	2	2.0	3.0	0.2	0.2	-	-
Fluorescer	0.18	0.15	0.5	0.3	0.2	0.2	0.2	0.2	0.2
Perfume	0.35	0.3	0.3	0.25	0.25	0.3	0.3	0.3	0.3
Moisture	&	Misc	-----	-----	to	100	-----	-----	-----

The Compositions are made as follows:

Composition M is made in the same way as Compositions A-D of Example 4 and has a similar density. For Composition E, all of the anionic surfactants together with some zeolite and carbonate are agglomerated in an inline mixer to form one component and the nonionic surfactant components are similarly agglomerated in a separate in line mixer. A 'minors' granule is formed of chelant, fluorescer, CMC and magnesium sulphate and the remaining components are added as dry mix materials or sprayed on as for compositions A-D in Example 4. This product has higher bulk density than that of Compositions A-D being at least 750 g/litre.

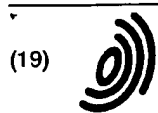
In Compositions F-L the anionic surfactants, Zeolite A, CMC, MA/AA polymer, chelant, carbonate, fluorescer and, where present, PVP and silicate, are incorporated in a spray dried granular component to which the remaining materials are dry mixed or sprayed on as appropriate. These spray dried granules can be further processed to achieve a predetermined product bulk density by e.g. communication or compaction by techniques and apparatus well known to those skilled in the art.

Claims

1. A solid detergent additive composition comprising a surface treated particulate, said particulate forming a substrate having a mean specific surface area in the range of from 0.05 to 0.9 m²/g and comprising a peroxyacid bleach precursor, said precursor containing one or more N- or O- acyl groups, the external surfaces of said substrate particulate being treated with and bearing a solid water soluble organic acid compound having a Mpt > 30 °C, said solid water soluble organic acid compound being in the form of a plurality of discrete coating particles adhered to the external surface of each substrate particle, characterised in that the discrete coating particles have a median particle size of no greater than 450 micrometers and wherein the surface treated particulate has a Coating Index value, defined by the ratio of the area of the coated external surface of the substrate to the area of the uncoated external surface of the substrate, in the range of from 0.01 to 9.
2. A solid detergent additive composition according to Claim 1 wherein the Coating Index value lies in the range of from 0.1 to 2, preferably from 0.2 to 1.0.
3. A solid detergent additive composition according to either one of Claims 1&2 wherein the median particle size of the particulate water soluble organic acid compound is no more than 150 micrometers, preferably no more than 100 micrometers.
4. A solid detergent additive composition according to any one of the preceding claims wherein the particulate water soluble organic acid compound is a monomeric or oligomeric carboxylate.
5. A solid detergent additive composition according to any one of the preceding claims wherein the particulate water soluble organic acid compound is a monomeric aliphatic polycarboxylic acid, preferably citric acid or an acid citrate salt.

6. A solid detergent additive composition according to any one of the preceding claims wherein the peroxyacid precursor material has a Mpt < 120 °C.
7. A solid detergent additive composition according to any one of the preceding claims wherein the peroxyacid precursor material is benzoyl caprolactam.
8. A solid detergent additive composition according to any one of Claims 1-7 wherein the substrate particulate comprises an agglomerate having a mean particle size in the range of from 250 to 1200 micrometers, preferably from 400 to 800 micrometers.
9. A solid detergent additive composition according to Claim 8 wherein the agglomerate comprises from 50 to 95% of the peroxyacid bleach precursor and from 5 to 50% of one or more components selected from binders, chelants, surfactants, soil suspending agents, fluorescers, suds suppressors, dye transfer inhibition agents, enzymes, water soluble organic and inorganic acid compounds and water insoluble inorganic compounds of high specific area.
10. An agglomerated detergent additive composition according to Claim 9 comprising a non aqueous organic binder material selected from C₁₂-C₁₈ fatty acids, C₁₂-C₁₈ aliphatic alcohols condensed with from 10 to 80 moles of ethylene oxide per mole of alcohol and polyethylene glycols of Mwt from 4000 to 10000, said binder material being present in an amount of from 5% to 25%, more preferably from 10% to 15% by weight of the composition.
11. An agglomerated detergent additive composition according to either one of Claims 9 & 10 wherein the water soluble acid compound is an organic acid compound preferably a monomeric or oligomeric carboxylate, more preferably a monomeric aliphatic polycarboxylate acid or an acid salt thereof, present in an amount of from 3 to 35% by weight of the agglomerate.
12. An agglomerated detergent additive composition according to any one of Claims 9-11 wherein the water insoluble inorganic compound is a zeolite or clay mineral having a surface area of 2-4m²/g and is present in an amount of from 1 to 15% by weight of the additive composition.
13. A solid detergent additive composition comprising surface-treated particulate according to any one of the preceding claims wherein the external surfaces of said substrate particulate are additionally treated with and bear a plurality of solid water insoluble inorganic compound particles of particle size <50 micrometers, more preferably of size 1-10 micrometers, said water insoluble inorganic compound particles being present in an amount of from 1 to 15% by weight of the additive composition.
14. A process for making a solid detergent additive composition comprising the steps of:
 - a) providing a solid peroxyacid bleach precursor material containing one or more N- or O- acyl groups having a Mpt >30 °C, said material being in the form of a mass of particles of median size <150 micrometers;
 - b) mixing therewith a solid organic binder material having a melting point >10 °C below the lower of the melting point or decomposition temperature of the bleach precursor;
 - c) treating said mixture to form agglomerates having a mean specific area in the range of from 0.05 to 0.9 m²/g;
 - d) maintaining said agglomerates at a temperature above the softening point of the organic binder material;
 - e) treating said agglomerates with a particulate water soluble organic acid compound of median particle size no greater than 450 micrometers; and
 - f) reducing the temperature of said treated agglomerates to a value in the range of from 10 °C to 25 °C to cause a plurality of discrete particles of said organic acid compound to adhere to the exterior surfaces of each of the agglomerates thereby to give a Coating Index value, defined by the ratio of coated to uncoated surface area of the agglomerates, in the range of from 0.01 to 9.
15. A process according to Claim 14 wherein the powdered water soluble organic acid compound has a mean particle size of <150 micrometers preferably less than 100 micrometers.

16. A process according to either one of Claims 14 and 15 wherein the solid peroxyacid precursor material has a Mpt <120 °C.
- 5 17. A process according to any one of Claims 14 to 16 wherein the solid peroxyacid precursor material is benzoyl caprolactam.
18. A process according to any one of Claims 14 to 17 wherein, in step a), a solid particulate water soluble organic acid material and a water insoluble inorganic compound of high specific surface area are mixed with said peroxyacid bleach precursor material.
- 10 19. A process according to Claim 18 wherein said particulate water soluble organic acid material is citric acid and the water insoluble inorganic compound is Zeolite A of surface area 2-4m²/g.
- 15 20. A process according to any one of Claims 14 to 19 wherein the organic binder material is selected from C₁₂-C₁₈ fatty alcohols condensed with from 10 to 80 moles of ethylene oxide per mole of fatty alcohol, polyethylene glycols of MWt from 4000 to 10000, C₁₂-C₁₈ fatty acids and polyvinyl pyrrolidone.
21. A process according to Claim 20 wherein the binder material is polyethylene glycol 4000.
- 20 22. A detergent composition comprising a surfactant material, a source of alkaline hydrogen peroxide and a solid detergent additive composition as claimed in any one of Claims 1-13 or a solid detergent additive composition as made by any one of Claims 14-21.
- 25 23. A solid detergent composition according to Claim 22 wherein the source of alkaline hydrogen peroxide is an inorganic perhydrate salt, preferably sodium perborate or sodium percarbonate.



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(54) **Detergent additive composition.**

(57) Detergent Additive compositions are disclosed in which a peroxyacid bleach precursor in the form of a substrate particulate having a mean specific area in the range of 0.05 to 0.9 m²/g, is coated with a solid particulate organic acid compound of median particle size <450 micrometers, so as to give a Coating Index value (CI) in the range of from 0.01 to 9. A process for making the additive compositions and detergent products containing them are also disclosed.

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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A,D	EP-A-0 191 396 (HENKEL KGAA) * the whole document *	1,14	C11D3/39 C11D17/00 C11D3/20 C11D11/00
A	EP-A-0 051 987 (PROCTER & GAMBLE ET AL.) * claims *	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C11D
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
BERLIN		19 September 1996	Pelli Wablat, B
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